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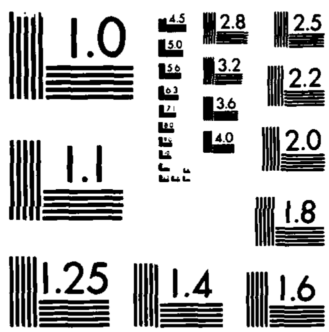

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MISCELLANEOUS PAPER SL-85-9

CHARACTERIZATION OF FOUR CLASS H HIGH SULFATE-RESISTANT PORTLAND CEMENTS

by

Alan D. Buck, Ronald E. Reinhold

Structures Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
PO Box 631, Vicksburg, Mississippi 39180-0631

US ARMY ENGINEER WATERWAYS EXPERIMENT STATION

September 1985

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Sulfate resistant cement

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

As part of the materials selection process for underground repository sealing of nuclear wastes, all available Class H high sulfate-resistant (HSR) portland cements that were commercially available in the United States in 1981 were obtained for testing and evaluation. Four such cements were found. The Class H designation is that used by the American Petroleum Institute; the HSR type is similar to a Type V portland cement as described in ASTM C 150 in that it is

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20. ABSTRACT (Continued).

intended to impart high sulfate resistance to the cement by the absence or near absence of calculated tricalcium aluminate (C_3A).

Each cement was characterized by a combination of chemical-physical testing and X-ray diffraction examination; it was concluded that all were generally similar and could be interchanged if such a need arose.

Preface

This report was prepared for the US Department of Energy (DOE) under continuing contract DE-AI97-81ET 46633. It was a milestone for FY 84 which was prepared as a draft report that was submitted in May 1984.

Mr. Steve Webster of the DOE in Columbus, Ohio, was Project Manager when this report was prepared for publication.

This report was prepared in the Concrete Technology Division (CTD) of the Structures Laboratory (SL), USAE Waterways Experiment Station (WES), by Mr. A. D. Buck under the direction of Mr. J. M. Scanlon, Chief, CTD, and Mr. Bryant Mather, Chief, SL. Mr. Buck was Project Leader in the CTD; Mr. R. E. Reinhold performed the physical testing of the cements and assisted overall.

Commander and Director of WES during the conduct of this study and the preparation of this report was COL Robert C. Lee, CE; Mr. Fred R. Brown was Technical Director. During publication of this report, COL Allen F. Grum, USA, was Director of WES; Dr. Robert W. Whalin was Technical Director.

Contents

Conversion Factors, Non-SI to SI (Metric)

Units of Measurement

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
gallons (US dry)	4.404884	cubic metres
pounds (mass)	0.4535924	kilograms
square centimetres per gram	0.1	square metres per kilogram

CHARACTERIZATION OF FOUR CLASS H HIGH SULFATE-RESISTANT PORTLAND CEMENTS

Background

1. As part of materials selection and evaluation in 1981 for this project, the producers of Class H sulfate-resistant oil-well cements were contacted. The intent was to obtain and test samples to show that it would or would not be feasible to use other sources than the one that had been used to that point.

2. There had been a general evolving consensus about the type of cement to use before that time as follows:

a. Expansive cementitious systems would be required for all or much of the sealing work. However, since expansive cements are essentially low-volume production specialty items without assured production from year to year, they would not be used. Instead, expansion would be obtained by addition of excess calcium sulfate to Type I portland cement. (This is essentially Class S expansive cement of ASTM C 845.)

b. Since some of the sealing for a salt repository would be in overlying anhydrite ($CaSO_4$) rock strata, this raised the possibility of sulfate attack on the hydraulic cementitious system. Therefore, a low C_3A* cement was needed to minimize any sulfate attack.

c. This meant that a Type V cement (which must not have over 5 percent C_3A) or a lower C_3A highly sulfate-resistant (HSR) Class H oil-well cement would be needed. The American Society for Testing and Materials (ASTM) cement specifications C 150 and the American Petroleum Institute (API) specifications for well cements (API Spec 10) are generally similar; however, there are some differences. The choice to use HSR Class H cement was made because the well-cementing industry expected to do the actual sealing work would be more familiar with API terminology, the HSR Class H specification has a maximum of 3 percent C_3A while an ASTM Type V can contain up to 5 percent C_3A, and finally a coarser ground cement would be preferable to inhibit hydration and set over the long working and pumping times likely to be needed for placement deep underground. The Type V cement has a minimum fineness requirement while the Class H cement does not have such a requirement and tends to be coarser than a Type V.

3. Finally, since the Concrete Technology Division is equipped to do cement testing by ASTM procedures and not by API procedures, it was decided that this testing would be by ASTM procedures. This was also preferable since they are widely used concensus standards rather than a limited usage single industry standard as with those of API.

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* Usual cement notation; C = CaO, A = Al_2O_3.

Samples

4. During March 1981, samples of cements intended to be HSR Class H oil-well cements were received from four producers and assigned Structures Laboratory (SL) serial numbers; they are identified below:

SL Serial No.	Amount	Producer
RC-868	Two bags (94-lb each)	Lone Star Industries, Sweetwater, Texas, Maryneal Plant
RC-869	Two 5-gal cans	Southwestern Portland Cement Co., Amarillo, Texas
RC-870	One cardboard drum (~200 lb)	Monarch Cement Co., Humboldt, Kansas
RC-871	Two 5-gal cans	General Portland Cement Co., Ft. Worth, Texas

Test procedure

5. The four cements purporting to be HSR Class H oil-well cements were tested in accordance with ASTM C 150, "Standard Specification for Portland Cement." In addition, analysis for Al_2O_3, Fe_2O_3, Mn_2O_3, TiO_2, P_2O_5, SrO, and BaO was made by atomic absorption spectrometry (AA). The major reason for doing this extra chemical work for each cement was to obtain better data for calculation of C_3A content since this is a low and critical value for these cements.

6. An as-received portion of each cement was examined by X-ray diffraction (XRD) to determine the phase composition. This examination was made in a sealed static nitrogen environment to minimize changes due to unintended hydration from exposure to moist air.

Results

7. The test reports (WES-85-81, WES-84-81, WES-88-81, WES-101-81) of the chemical and physical data that were obtained by ASTM C 150 testing are shown as Tables 1 through 4 for cements RC-868, 869, 870, and 871, respectively. It is important to realize that the type of testing that was done cannot show that the cements met the API specification requirements they were intended to meet. However, examination of the data does not indicate or suggest that they would not be HSR Class H oil-well cements. Calculated C_3A contents ranged from 1 to 3 percent, air permeability fineness ranged from 2220 to 2730 cm^2/g (222 to 273 m^2/kg), and the other chemical and physical data were similar for all four cements.

8. Several earlier shipments of the same HSR Class H cement from the Maryneal Plant were received, tested, and used in other or in related work.

Data for RC-853 are shown in Table 1 of Reference 1. Data for RC-853(2) are shown on pages 31, 39, and 48 through 50 in Reference 2. The data for repetitive shipments have been similar enough to indicate no more than normal variation within different lots of a single material.

9. XRD showed the four cements to be similar. All were high alite and low belite, the aluminoferrite was always C_6AF_2, and C_3A was not detected (RC-868) or was possibly present at a low level in the other three cements. The small amounts of calcium sulfate added to regulate time of setting of the cements were present as gypsum ($CaSO_4 \cdot 2H_2O$) in cements RC-869, 870, and 871; it was probably present in RC-868 as anhydrite ($CaSO_4$) or calcium sulfate hemihydrate ($CaSO_4 \cdot 1/2H_2O$) which are more difficult to detect because of interference with cement XRD peaks. Small amounts of free lime (CaO) or periclase (MgO) were sometimes possibly present. However, autoclave tests did not show excessive expansion (Tables 1 through 4). The small differences in amounts of minor compounds that were found in the four cements by XRD would not be expected to have a significant impact on their performance.

Discussion

10. Comparative examination of four cements by conventional ASTM cement testing procedures showed all to be similar; this was also borne out by XRD.

11. Comparison with previous data for one of the cements showed it had been essentially the same for several years of production.

12. While the testing was not suited to specification verification of the four cements as API, HSR Class H oil-well cements, the present and past tests did indicate consistency of production within one source and enough similarity between sources to permit substitution of one cement for another without significant problems.

Conclusion

13. The present testing and examination of four cements intended to be HSR Class H oil-well cements indicate that different sources of this material can be used if this becomes desirable.

References

1. Buck, A. D.; Rhoderick, J. E.; Burkes, J. P.; Mather, K; Reinhold, R. E.; and Boa, J. A., Jr., "Modification of Bell Canyon Test (BCT) 1-FF Grout," WES Miscellaneous Paper SL-83-18 (also SAND 83-7097), Sep 1983, Vicksburg, Miss.

2. Roy, D. M.; Grutzeck, M. W.; Mather, K.; and Buck, A. D., "PSU/WES Interlaboratory Comparative Methodology Study of An Experimental Cementitious Repository Seal Material," WES Miscellaneous Paper SL-81-2, Report 2, Final Results, Mar 1982, Vicksburg, Miss.

Table 1

TO:		FROM: CORPS OF ENGINEERS U. S. ARMY
Structures Laboratory WES ATTN: Mrs. K. Mather	REPORT OF TESTS OF PORTLAND CEMENT RC-868	Structures Laboratory Waterways Exp Station ATTN: Cem & Pozz Group P. O. Box 631 Vicksburg, MS 39180

TEST REPORT NO. WES-85-81 | BIN NO. | CWT REPRESENTED | DATE: 1 April 81

SPECIFICATION: Class H Oil Well | DATE SAMPLED:

COMPANY: Lone Star | LOCATION: Maryneal, TX | BRAND:

THIS CEMENT DOES MEET SPECIFICATION REQUIREMENTS

SAMPLE NO.	WET				AA	PLASMA	COLOR-	
SiO_2, %	22.44					EMISSION	METRIC	
Al_2O_3, %	3.76*			Al_2O_3	3.60			
Fe_2O_3, %	3.91							
MgO, %	2.57			Fe_2O_3	3.91			
SO_3, %	2.05							
LOSS ON IGNITION, %	0.51							
ALKALIES-TOTAL AS Na_2O, %	0.52							
Na_2O, %	0.15							
K_2O, %	0.56							
INSOLUBLE RESIDUE, %	0.14			TiO_2	0.17			
CaO, %	63.66							
C_3S, %	52			P_2O_5			0.05	
C_3A, %	3							
C_2S, %	25			Mn_2O_3	0.02			
$C_3A + C_3S$, %								
C_4AF, %	12			SrO		0.06		
$C_4AF + 2C_3A$, %	19			BaO		0.03		
Total **	99.80							
HEAT OF HYDRATION, 28D, CAL G								
SURFACE AREA, SQ CM G (A P I)	2220							
AIR CONTENT, %	9.0							
COMP. STRENGTH, 3 D, PSI	1610							
COMP. STRENGTH, 7 D, PSI	1970							
COMP. STRENGTH, 28 D, PSI	2940							
Density	3.22	Mg/m^3						
SAMPLE NO.								
AUTOCLAVE EXP., %	0.00							
INITIAL SET, HR/MIN	4:35							
FINAL SET, HR/MIN	7:05							
SAMPLE NO.								
AUTOCLAVE EXP., %								
INITIAL SET, HR/MIN								
FINAL SET, HR/MIN								

REMARKS: $*Al_2O_3 = R_2O_3 - (Fe_2O_3 + TiO_2 + P_2O_5)$

$**$Total does not include Mn_2O_3, SrO, BaO

W. G. Miller

W. G. MILLER
Chemist
Chief, Cement & Pozzolan Group

ENG FORM 1 MAR 77 6008-R

Table 2

TO:		FROM: CORPS OF ENGINEERS U. S. ARMY
Structures Laboratory WES ATTN: K. Mather	REPORT OF TESTS OF PORTLAND CEMENT RC-869	Structures Laboratory Waterways Exp Station ATTN: Cem & Pozz Group P.O. Box 631 Vicksburg, MS 39180

TEST REPORT NO. WES-84-81 | BIN NO. | CWT REPRESENTED: | DATE: 1 April 81

SPECIFICATION: Class H Oil Well | DATE SAMPLED:

COMPANY: Southwestern | LOCATION Amarillo, TX | BRAND:

THIS CEMENT DOES MEET SPECIFICATION REQUIREMENTS

SAMPLE NO.	WET				AA	PLASMA	COLORIMETRIC	
SiO_2, %	23.50					EMISSION		
Al_2O_3, %	2.85*							
Fe_2O_3, %	3.01			Al_2O_3	2.79			
MgO, %	1.43							
SO_3, %	2.45			Fe_2O_3	3.08			
LOSS ON IGNITION, %	1.16							
ALKALIES-TOTAL AS Na_2O, %	0.23							
Na_2O, %	0.16							
K_2O, %	0.10							
INSOLUBLE RESIDUE, %	0.14			TiO_2	0.15			
CaO, %	64.83							
C_3S, %	55			P_2O_5			0.16	
C_3A, %	2							
C_2S, %	26			Mn_2O_3	0.02			
$C_3A + C_3S$, %								
C_4AF, %	9			SrO		0.07		
$C_4AF + 2 C_3A$, %	14			BaO		0.15		
Total **	9[illegible].79							
HEAT OF HYDRATION, 28D, CAL/G								
SURFACE AREA, SQ CM/G (A.P.)	2670							
AIR CONTENT, %	7.2							
COMP. STRENGTH, 3 D, PSI	1520							
COMP. STRENGTH, 7 D, PSI	2100							
COMP. STRENGTH, 28 D, PSI	3890							
Density	3.16	Mg/m^3						
SAMPLE NO.								
AUTOCLAVE EXP., %	-0.02							
INITIAL SET, HR/MIN	4:00							
FINAL SET, HR/MIN	7:00							
SAMPLE NO.								
AUTOCLAVE EXP., %								
INITIAL SET, HR/MIN								
FINAL SET, HR/MIN								

REMARKS: * $Al_2O_3 = R_2O_3 - (Fe_2O_3 + TiO_2 + P_2O_5)$

** Total does not include Mn_2O_3, SrO, BaO

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ENG FORM 1 MAR 72 6008-R

Table 3

TO:		FROM CORPS OF ENGINEERS U.S. ARMY
Structures Laboratory ATTN: K. Mather	REPORT OF TESTS OF PORTLAND CEMENT RC-870	Structures Laboratory Waterways Experiment Station ATTN: Cem & Pozz Group P.O. Box 631 Vicksburg, MS 39180

TEST REPORT NO. WES-88-81	BIN NO.	CWT REPRESENTED	DATE 3 April 81
SPECIFICATION: Class H Oil Well		DATE SAMPLED:	
COMPANY: Monarch Cem Co.	LOCATION: Humboldt, KS		BRAND:
THIS CEMENT DOES MEET SPECIFICATION REQUIREMENTS			

SAMPLE NO.	WET				AA	PLASMA	COLOR	
SiO_2, %	22.16					EMISSION	METRIC	
Al_2O_3, %	3.35*			Al_2O_3	3.24			
Fe_2O_3, %	4.27							
MgO, %	2.25			Fe_2O_3	~~4.23~~			
SO_3, %	2.29							
LOSS ON IGNITION, %	1.17							
ALKALIES-TOTAL AS Na_2O, %	0.55							
Na_2O, %	0.25							
K_2O, %	0.46			TiO_2	0.18			
INSOLUBLE RESIDUE, %	0.13							
CaO, %	63.83			P_2O_5			~~0.08~~	
C_3S, %	56							
C_3A, %	2			Mn_2O_3	~~0.14~~			
C_2S, %	21			SrO		0.18		
$C_3A + C_3S$, %				BaO		0.01		
C_4AF, %	13							
$C_4AF + 2C_3A$, %	16							
TOTAL **	100.29							
HEAT OF HYDRATION, 28D, CAL/G								
SURFACE AREA, SQ CM/G (A.P.)	2730							
AIR CONTENT, %	8.6							
COMP. STRENGTH, 3 D, PSI	1630							
COMP. STRENGTH, 7 D, PSI	2120							
COMP. STRENGTH, 28 D, PSI	3090							
Density	3.20	Mg/m^3						
SAMPLE NO.								
AUTOCLAVE EXP., %	0.04							
INITIAL SET, HR/MIN	3:00							
FINAL SET, HR/MIN	4:35							
SAMPLE NO.								
AUTOCLAVE EXP., %								
INITIAL SET, HR/MIN								
FINAL SET, HR/MIN								

REMARKS: $*Al_2O_3 = R_2O_3 - (Fe_2O_3 + P_2O_5 + TiO_2)$

**Total - Mn_2O_3, SnO & BaO not included.

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Table 4

TO:	REPORT OF TESTS OF PORTLAND CEMENT	FROM: CORPS OF ENGINEERS U. S. ARMY
Structures Laboratory WES ATTN: K. Mather	RC-871	Structures Laboratory Waterways Exp Station ATTN: Cem & Pozz Group P.O. Box 631 Vicksburg, MS 39180

TEST REPORT NO. WES-101-81	BIN NO.	CWT REPRESENTED.	DATE. 1 April 81
SPECIFICATION: Class H Oil Well		DATE SAMPLED:	
COMPANY: General Portland	LOCATION Ft. Worth, TX		BRAND.

THIS CEMENT DOES MEET SPECIFICATION REQUIREMENTS

SAMPLE NO.	WET				AA	PLASMA	COLOR-	
SiO_2, %	20.60					EMISSION	METRIC	
Al_2O_3, %	4.37*			Al_2O_3	4.36			
Fe_2O_3, %	6.37							
MgO, %	1.43			Fe_2O_3	6.50			
SO_3, %	1.66							
LOSS ON IGNITION, %	1.02							
ALKALIES-TOTAL AS Na_2O, %	0.29							
Na_2O, %	0.33							
K_2O, %	0.29							
INSOLUBLE RESIDUE, %	0.15			TiO_2	0.17			
CaO, %	63.35							
C_3S, %	58			P_2O_5			0.16	
C_3A, %	1			Mn_2O_3	0.14			
C_2S, %	15							
$C_3A + C_3S$, %				SrO		0.12		
C_4AF, %	19			BaO		0.02		
$C_4AF + 2C_3A$, %	21							
Total **	99.66							
HEAT OF HYDRATION, 28D, CAL/G								
SURFACE AREA, SQ CM/G (A.P.)	2320							
AIR CONTENT, %	9.9							
COMP. STRENGTH, 3 D, PSI	1060							
COMP. STRENGTH, 7 D, PSI	1720							
COMP. STRENGTH, 28 D, PSI	2130							
Density	3.17	Mg/m^3						
SAMPLE NO.								
AUTOCLAVE EXP., %	0.00							
INITIAL SET, HR/MIN	3:40							
FINAL SET, HR/MIN	5:15							
SAMPLE NO.								
AUTOCLAVE EXP., %								
INITIAL SET, HR/MIN								
FINAL SET, HR/MIN								

REMARKS: $*Al_2O_3 = R_2O_3 - (Fe_2O_3 + TiO_2 + P_2O_5)$

$**$Total Mn_2O_3, SrO, and BaO not included

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